MODELLING THE EFFECTS OF MOTOR VEHICLE EMISSIONS ON PHOTOCHEMICAL SMOG IN THE PERTH AIRSHED

Environmental Engineering Honours Project
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How important clean air is to life becomes apparent when considering the fact that humans can do without food for up to 40 days, without air however, only a few minutes...

(Baumbach 1996)
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ABSTRACT

Photochemical smog is now considered to be one of the most significant pollution problems facing many cities of the world. Formation of photochemical smog requires three main ingredients: nitrogen oxides (NO$_X$), volatile organic compounds (VOCs) and ample sunlight (hv). These three components combined with stable atmospheric conditions lead to the formation of ground-level ozone (O$_3$). Episodes of photochemical smog with O$_3$ concentrations exceeding 100ppb can cause serious health problems such as lung-tissue damage, reduction of lung function and sensitising of lungs to the effects of other irritants.

An explicit West Australian tropospheric photochemical model was developed to simulate the development of ozone in the Perth airshed using data from the Perth Photochemical Smog Study (PPSS). The mathematical model simulates the tropospheric degradation and resultant secondary pollutant formation from emitted VOCs and NO$_X$. The model has been updated with emissions data from the most recent Perth airshed inventory (1998/1999 reporting period). Parameters have been adjusted to more realistically replicate the NO$_X$, VOC and CO emissions throughout the day. The temperature parameter has been modified to replicate the profile of a Perth hot summers day. A comparison between the 1992/1993 and 1998/1999 model outputs of maximum possible ozone concentrations corresponded to an increase from 141ppb to 148ppb. The airshed was further determined to be NO$_X$-limited.

Three unique scenarios were developed to forecast changes in O$_3$ concentration in the Perth airshed in 10 years time. Scenario 1 represents the current trend of emission increases. Scenario 2 represents a dramatic increase of NO$_X$ emissions and Scenario 3 looks at the effects of implementing NO$_X$ control with an actual reduction in NO$_X$ emissions. The peak O$_3$ concentrations for Scenario 1, 2 and 3 were 165ppb, 209ppb and 142ppb respectively.
The PPSS confirmed that motor vehicle emissions are the dominant cause of Perth’s smog, being the largest source of NO\textsubscript{X} and reactive VOCs. Aromatic hydrocarbons represent a major component of vehicle exhaust emissions with a number of these species considered carcinogenic. The six main groups of aromatic hydrocarbons found in vehicle exhaust emissions are: toluene, benzene, xylenes, ethyl toluene, ethyl benzenes and tri-methyl benzenes. The effect of these components on the simulated O\textsubscript{3} profiles was further investigated. Each aromatic group was removed one at a time from the airshed VOC emissions of Scenario 2 and Scenario 3.

The process of assessing the effect of removing an individual species under projected scenarios, as compared to injecting an additional mass of the individual species under current conditions (e.g. POCP testing), represents an innovative technique of determining the overall impact of a species on the level of ozone generated. In this way of testing, policy and control techniques can effectively target and restrict individual species that make the largest impact on ozone generation throughout the day. The results provide confirmation that choice of policy focus needs to be continually assessed as airshed emissions change over time.

To reduce peak ozone concentrations, there is a need to control the dominant source of NO\textsubscript{X} and VOC emissions within the Perth airshed. A combination of policy and technology are successfully reducing motor vehicle emissions by reducing maximum allowed emissions from new vehicles (ADRs) and strict legislation of cleaner fuel quality. Offsetting these improvements in emissions reduction is the ever-increasing car population in combination with increased kilometres travelled. Smart urban planning consisting of improved community layout and effective public transit need to be enhanced to reduce the reliance of cars within the Perth metropolitan area.
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GLOSSARY

Airshed: The area within which the pollutants are generated, dispersed and deposited.

Emission Inventory: Gives a breakdown by significant sources, of the estimated total mass of specific air pollutants emitted in a study area for a given year.

Mixing Height: During the day solar radiation warms the ground, which in turn warms air near the ground surface. Such air tends to rise by buoyant forces until it reaches a height where its temperature (and hence density) are equal to that of the surrounding air. This height is called the mixing height.

Boundary Layer: The layer of air between the mixing height and the ground within which atmospheric mixing is aided by buoyancy.

Primary Pollutant: Pollutants which are emitted directly from their sources of emission (i.e. CO from vehicular exhaust).

Secondary Pollutant: Pollutants which are formed (either by condensation, decomposition or chemical reaction) from other primary pollutants after they have been emitted into the environment.

Precursor Reactants: Emitted compounds that react in sunlight to form ozone or other photochemical oxidants.

NO\textsubscript{X}: Nitrogen oxides (Nitric oxide & Nitrogen dioxide)

NO\textsubscript{Z}: Represents gaseous oxygenated nitrogen species including nitric acid (HNO\textsubscript{3}), peroxyacetyl nitrate (PAN) and other gaseous organic nitrates (not including NO\textsubscript{X}).

VOC: Volatile organic compound

CO: Carbon monoxide

POCP: Photochemical Ozone Creation Potential

NPI: National Pollutant Inventory – An internet database designed to provide the community with information on the type and amount of certain chemicals being emitted to the environment.

EPA: Environmental Protection Authority

DoE/DEP: Department of Environment (formerly Department of Environmental Protection)

NEPC: National Environment Protection Council

PPSS: Perth Photochemical Smog Study

ppb: parts per billion
1. INTRODUCTION

Perth is a great place to live. One of the main attractions of living in Perth is the great weather, which includes the long hot summers. Consequently there is a strong attraction to the coastal lifestyle and this is the reason we see the city of Perth stretch in a north-south corridor from Butler in the north to Mandurah in the south, with the beach providing the western boundary.

Another attraction of Perth residents is low-density living, big homes with big backyards on big properties. Perth’s long hot summers and the attraction of living by the beach, combined with the appeal of large low-density residential homes have contributed to Perth becoming a sprawling city.

Urban sprawl is associated with limited public transport access, travelling greater distances to satisfy work and social requirements, increased road congestion, traffic delays and high dependence on motor vehicles. Perth is one of the most car-dominated cities in the world with Western Australia having the highest rate of vehicle ownership in Australia.

In a study on photochemical smog carried out in 1996, it was found that motor vehicle emissions are the dominant cause of photochemical smog, being the largest source of precursor reactants (nitrogen oxides and volatile organic compounds). These emissions combined with ample sunlight, strong temperatures and increasing motor vehicle usage leads to the serious air pollution problem of photochemical smog.

The objectives of this honours project included:

- Analysis of emissions from the latest Perth airshed inventory,
- Modelling the detailed tropospheric chemistry that results from these emissions,
- Making predictions for emission rates in ten years time and modelling of these forecast scenarios,
- Analysis of the contribution to ozone formation from singular aromatic compounds found in motor vehicle exhaust emissions, and
- Researching current policy and control strategies in place to reduce the dominant cause of photochemical smog within the Perth airshed.
2. LITERATURE REVIEW

2.1 PHOTOCHEMICAL SMOG

2.1.1 What is Photochemical Smog?

Formation of photochemical smog requires three main ingredients:
1. Nitrogen oxides (NO\textsubscript{X}),
2. Volatile organic compounds (VOCs), and
3. Ample sunlight (hv)

Ample sunlight is necessary for the initiation of crucial photolysis reactions. Stable atmospheric conditions are also required so that precursor reactants are not quickly diluted.

Photochemical smog is characterised by high concentrations of ground-level ozone (O\textsubscript{3}) and consequently, ozone concentration is used to measure the magnitude of smog episodes. Other elements of photochemical smog include:
- Aldehydes (RCHO),
- Peroxy acetyl nitrate (PAN),
- Nitric acid (HNO\textsubscript{3}), and
- Nitrate aerosols.

Photochemical smog consists mainly of gases that are generally invisible at low concentrations. At higher concentrations, condensed smog particulates remain suspended in the air, and are typified by a whitish haze as seen in Figure 1:

![Perth Skyline (DPI 2003b)](image)

**Figure 1: Perth Skyline (DPI 2003b)**
2.1.2 Ozone (O₃)
More than 90% of the irritating and oxidising properties of photochemical smog are due to ozone (O₃) (Griffith University 2001). Ozone is a colourless, highly reactive gas with a distinct odour. Ozone (O₃) is formed when excited oxygen atoms (O⁺) combine with reactive oxygen molecules (O₂):

\[ O^+ + O_2 \rightarrow O_3 \]

2.1.3 Nitrogen Oxides (NOₓ)
Collectively nitric oxide (NO) and nitrogen dioxide (NO₂) gases are referred to as nitrogen oxides (NOₓ). Nitrogen oxides (NOₓ) irritate lungs and can lower immunity to respiratory infections. Exposure to high levels of NOₓ has proven to cause severe lung injury (DoE 2005b).

Nitric oxide (NO) is a colourless and odourless gas that is produced whenever a fuel is burned in air with a hot flame. The reaction between nitrogen (N₂) and oxygen (O₂) molecules is negligibly slow except at very high temperatures such as those that occur in the modern combustion engines of motor vehicles (Baird & Cann 2005).

\[ N_2 + O_2 \rightarrow \text{hot flame} \rightarrow 2NO \]

Nitrogen dioxide (NO₂) is a reddish-brown, pungent, acidic gas that is corrosive and strongly oxidising. Unlike many other molecules, the atomic structure of NO₂ allows it to absorb energy from sunlight. This absorbed sunlight gives the NO₂ molecules extra energy, causing them to split into NO molecules and energetic O⁺ atoms.

\[ \text{NO}_2 + \text{Sunlight} \rightarrow \text{NO} + \text{O}^+ \]

2.1.4 Volatile Organic Compounds (VOCs)
Volatile organic compounds (VOCs) is a term frequently used to include all vapour-phase organic species in the atmosphere. VOCs are emitted in substantial quantities from both biogenic and anthropogenic sources and have a major influence on the chemistry of the lower atmosphere (Saunders et al. 2003). VOCs are produced from combustion and are emitted from motor vehicles and a variety of industrial and domestic sources.
VOCs are predominantly hydrocarbon compounds and are known as air ‘toxins’ or hazardous air ‘pollutants’. Some VOCs are known to contribute to the formation of photochemical smog, ozone depletion and also pose as a risk to human health.

2.1.5 Ozone Isopleth Diagrams
An ozone isopleth diagram represents the dependence of ozone production on the availability of VOC and NO$_X$ for a given area. An isopleth is a line of constant concentration, which shows the maximum ozone concentration achieved as a function of different VOC and NO$_X$ levels. Isopleth diagrams differ from one urban region to another because of differences in meteorology and source emissions. An example of an isopleth diagram is shown in Figure 2:

![Figure 2: Example of an Ozone Isopleth Diagram (Baird & Cann 2005)](image)

2.1.6 Human health
Episodes of photochemical smog with ozone concentrations exceeding 100 ppb can cause serious health problems such as lung-tissue damage, reduction of lung function and the sensitising of lungs to the effects of other irritants (DoE 2003; Baird & Cann 2005). Exercise appears to exacerbate the effects of ozone on lung function (NEPC 1998). Acute effects such as coughing, dryness of the throat, wheezing and chest tightness have been observed in some people after exposures to ozone of less than an hour (Rubin 2001; DoE & Main Roads WA 2000).
Other photochemical smog oxidants including peroxy acetyl nitrate (PAN), nitric acid (HNO$_3$) and aldehydes (RCHO) are all strong irritants of the eyes, nose and throat (DEP & Western Power 1996).

2.1.7 Environmental Concerns

Ground-level ozone interferes with the ability of plants to produce and store food by damaging their leaves and consequently reducing their ability to photosynthesise (DEP & Western Power 2000). This leads to reduced growth rates and as a result, the plants are more susceptible to disease, insect attack and less tolerant to cold temperatures and the effects of other environmental pollutants (DEP & Main Roads WA 2000).

At current levels the impact of ozone on plant life within Western Australia is not well understood, however, it has been estimated that ozone has lead to a 5-10% decline in crop yields in the United States of America (DEP & Main Roads WA 2000).

2.1.8 Atmospheric Structure - Troposphere vs. Stratosphere

Within the troposphere, temperature decreases at a rate of approximately 6.5°C per 1000 metres up to an altitude of about 11,300 metres (the lower bound of the stratosphere). At that height, the temperature becomes constant at –55°C. The constant temperature of the lower stratosphere greatly inhibits vertical mixing (Hemond & Fechner-Levy).

It is important to make a distinction between the ozone in photochemical pollution at ground-level within the troposphere and ozone in the stratosphere, where its presence in the “ozone layer” plays a crucial role in absorbing ultraviolet radiation emitted by the sun (Rubin 2001).

Approximately 85-90% of the earth’s atmospheric ozone is found in the stratosphere (Rubin 2001). Ozone does occur naturally in the troposphere, however at much lower concentrations than found in the stratosphere. Tropospheric ozone concentrations in unpolluted, remote regions are currently 15 to 35 ppb (Lefohn et al. 1990).
2.1.9 Chemistry of Photochemical Smog Formation

The ozone formation process starts when absorbed sunlight gives nitrogen dioxide (NO₂) molecules extra energy, causing them to split into nitric oxide (NO) molecules and energetic oxygen atoms (O⁺) as seen in Equation #1. The main source of O⁺ atoms in the troposphere comes from this photochemical dissociation (Baird & Cann, 2005):

Equation #1: \[ \text{NO}_2 + \text{Sunlight} \rightarrow \text{NO} + \text{O}^+ \]

The excited O⁺ atoms seek reaction partners. The most abundant molecules found within the troposphere are nitrogen (N₂), however these molecules are inert. The second most abundant molecules are oxygen (O₂) which are much more reactive than N₂. The O⁺ atoms rapidly combine with the reactive O₂ molecules to form ozone (O₃) as per Equation #2:

Equation #2: \[ \text{O}^+ + \text{O}_2 \rightarrow \text{O}_3 \]

Equation #1 and #2 represent the most significant path for ozone (O₃) formation. The ozone created in Equation #2 is also chemically reactive, and readily combines with urban emissions of NO as per Equation #3:
High concentrations of ozone (O$_3$) are therefore prevented from developing in the presence of significant NO by the reaction in Equation #3.

For high O$_3$ levels to occur, other reactions are required which remove NO from the urban atmosphere. This perturbation of the natural ozone cycle is provided by a series of reactions involving reactive hydrocarbons, as shown in the following equations.

Not only do excited O* atoms react with plentiful O$_2$ molecules, they also tend to react with other atmospheric species such as abundant H$_2$O molecules (water vapour), to form hydroxyl radicals (’OH) as seen in Equation #4:

\[
\text{Equation #4: } O + H_2O \rightarrow 2'OH
\]

The hydroxyl free radical (’OH) is the key reactive species in the troposphere (Baird & Cann 2005). Because free radicals are missing an electron, they react readily trying to gain the missing electron to achieve a more stable state. The hydroxyl radical does not react with molecular oxygen; however it does react with most other species in the atmosphere, including hydrocarbons (Rubin 2001). There are hundreds of different hydrocarbon compounds in the atmosphere, all with varying degrees of reactivity. The hydroxyl radical (’OH) attacks practically all of these compounds initiating their chemical oxidation.

The reactions that follow the initial attack of a hydroxyl radical on a large hydrocarbon molecule are quite complex but follow similar patterns as for smaller molecules (Rubin 2001). The hydrocarbon that is attacked could be one of a large variety commonly found in urban areas (e.g. propane, hexane, benzene, toluene, xylene or hydrocarbons of natural origin such as isoprene).

The hydroxyl radical attack on a small hydrocarbon like methane (CH$_4$), results in the removal of a hydrogen atom and the formation of an organic radical (’CH$_3$) and water molecule (H$_2$O) as seen in Equation #5:

\[
\text{Equation #5: } CH_4 + 'OH \rightarrow 'CH_3 + H_2O
\]
This reaction is the first step in atmospheric oxidation. By destroying the hydrocarbon molecules, hydroxyl radicals (which convert to stable water vapour) prevent hydrocarbons from accumulating in the atmosphere, thus acting as a type of hydrocarbon cleaning agent (Rubin 2001).

This reaction however, also initiates a new chain of radical reactions. In this case, the ‘victim’ of the hydroxyl radical attack (CH₄) is now missing one electron and has become a free radical itself (·CH₃). This new methyl radical (·CH₃) is also reactive and seeks another molecule to react with. The O₂ molecule is once again the best candidate. In this reaction (Equation #6), yet another radical (CH₃O₂•) is formed:

Equation #6: 
\[ \cdot{\text{CH}}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2\cdot + \text{M} \]

*Note: “M” in this reaction refers to another air molecule (e.g. nitrogen or oxygen) needed to absorb some of the energy released in the reaction.*

The CH₃O₂• radical can react with a variety of species, but its reaction with NO (as seen in Equation #7) is extremely important for the creation of photochemical smog:

Equation #7: 
\[ \text{CH}_3\text{O}_2\cdot + \text{NO} \rightarrow \text{CH}_3\text{O}\cdot + \text{NO}_2 \]

This reaction creates one more free radical (CH₃O•). It also converts one molecule of NO to NO₂; this being the important path by which NO is oxidised to NO₂ without involving O₃ (as seen in Equation #3).

The CH₃O• radical then reacts with O₂ (as seen in Equation #8) to form formaldehyde (HCHO) and the hydroperoxyl radical (HO₂•):

Equation #8: 
\[ \text{CH}_3\text{O}\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2\cdot \]

Equation #9 illustrates the overall result of the four preceding reactions:

Equation #9: 
\[ \text{CH}_4 + \cdot{\text{OH}} + \text{NO} \rightarrow \text{HCHO} + \text{HO}_2\cdot + \text{NO}_2 \]

This result shows that the photochemical oxidation of hydrocarbons leads to the conversion of NO to NO₂. By converting one species that destroys ozone (NO) to one that produces it (NO₂), hydrocarbons provide the fuel for the NOₓ photochemical-cycle that produces ozone (O₃).
2.2 PERTH PHOTOCHEMICAL SMOG STUDY (PPSS)

2.2.1 Overview of PPSS

Photochemical smog measurements commenced in Perth in 1989 at a single location in Caversham (15 kilometres north east of Perth city). Measurements taken over the first summer period revealed smog levels that exceeded the guidelines recommended by the National Health and Medical Research Centre (NHMRC) (DEP & Western Power 1996).

An application to increase the capacity of one of Western Power’s gas turbine power stations was received by the Environmental Protection Authority (EPA) in 1991 (DEP & Western Power 1996). The power station in question was located in Pinjar (40 kilometres north of Perth city). The EPA expressed concerns that increased NO\textsubscript{X} emissions from the station would contribute to Perth’s emerging photochemical smog problem.

Before approval of the upgrade could be granted, Western Power was to undertake a study of the formation and distribution of photochemical smog in Perth. This study was to be used as an aid in determining the potential impact of increased NO\textsubscript{X} emissions from the power station.

The \textit{Perth Photochemical Smog Study} (PPSS) was developed as a jointly operated and managed project, funded by Western Power and with the Department of Environment (DoE) contributing facilities and scientific expertise. The primary objective of the PPSS was to measure the magnitude and distribution of photochemical smog concentrations experienced in the Perth region. The study commenced in early 1992 and was completed by May 1996.

The Perth airshed study region is represented in Figure 4. The study region encompasses an area of approximately 8,600 square kilometres. This region includes the extremities of metropolitan Perth and incorporates all industrial and commercial premises expected to influence Perth’s air quality (DEP 2002).
The major sources of emissions, which lead to the formation of photochemical smog, were quantified into four categories, as follows:

1. **Motor Vehicles** – Includes emissions from on-road vehicles including passenger vehicles, light commercial vehicles, motorcycles, light trucks and heavy-duty vehicles.

2. **Industrial Emissions** – This refers to emissions from larger commercial facilities. Examples include petroleum refineries, bulk storage facilities, construction facilities and chemical manufacture operations.

3. **Area-Based Sources** – Includes domestic activities and small commercial facilities including a wide range of sources, such as service station fuel vapour losses, domestic solid fuel combustion, motor vehicle refinishing and marine craft. Individually these emission sources tend to be minor.

4. **Biogenic Emissions** – Represents emissions of reactive organic species from vegetation, which can be significant in the photochemical smog process.
2.2.2 PPSS - Significant Findings
The PPSS was the first time that the magnitude and distribution of photochemical smog within the Perth region had been measured. Significant findings from the three-year study included (DEP & Western Power 1996):

- The air over Perth on most summer days is relatively clean, due to the windy climate and isolation from other cities.
- There is a dominant, well-defined weather pattern related to Perth’s smog events.
- On average there were ten days per year where peak hourly ozone concentrations exceeded the NHMRC goal of 80ppb.
- Each of the monitoring sites used in the PPSS (covering an area extending from Rottnest to Rolling Green and Gingin to Rockingham), recorded exceedances of 80ppb during the study, confirming that ozone events occurred across a large region surrounding the city.
- Ozone events tended to be of short duration (an hour or two). This contrasts with regions of the USA and Europe, where elevated ozone levels are experienced over many days, caused by the transport of pollutants from distant cities and industrial areas.
- The inventory of smog precursor emissions, coupled with modelling results, confirmed that motor vehicles are the dominant cause of Perth’s smog, being the largest source of NO\textsubscript{X} and reactive VOCs.

2.2.3 1998/1999 Airshed Emissions Inventory Update
As the PPSS emissions inventory was developed around the 1992/1993 financial year, it was timely to update the Perth region emissions inventory (DEP 2002):

**NO\textsubscript{X} Emissions**
An estimated 70,253 tonnes of NO\textsubscript{X} were emitted in the Perth airshed during the 1998/1999 reporting period, an increase of 15,376 tonnes compared to the 1992/1993 inventory.
VOC Emissions
The total mass of VOCs emitted into the Perth airshed during the 1998/1999 reporting period was estimated to be 69,661 tonnes, a decrease of 11,397 tonnes compared to the 1992/1993 inventory.

CO Emissions
An estimated 283,336 tonnes of CO were emitted in the Perth airshed during the 1998/1999 reporting period, a decrease of 2,803 tonnes from the 1992/1993 inventory.

ISO Emissions
The estimated emissions from biogenic and natural sources for both 1992/1993 and 1998/1999 were assumed to be the same, at 16,000 tonnes per year.

![Comparison of Annual Emissions](image)

**Figure 5:** Comparison of annual emissions between the 1992/93 and 1998/99 emission inventories
2.3 CITY OF PERTH

2.3.1 Meteorology

The highest smog concentrations are measured on those days during spring to autumn when a weak low-pressure trough is situated very close to the coast (as seen in Figure 6) and subsequently crosses the coast in the afternoon (DEP & Western Power 1996).

Under these conditions, emissions from morning peak hour traffic are blown offshore by north easterly winds where smog reactions proceed under high temperatures. A strong temperature inversion exists under these conditions, which keeps the smog plume concentrated near the ocean surface under stable atmospheric conditions. A weak sea breeze in the afternoon returns the stable offshore air mass across the metropolitan area where it receives an additional boost of smog reactants from afternoon peak-hour traffic emissions (DEP & Western Power 1996).

Figure 6: Pressure Chart
Example of a Coastal Low-Pressure Trough
(DEP & Western Power 1996)

Figure 7: Schematic of Ozone Formation over Perth city (DEP & Main Roads WA 2000)
2.3.2 Population growth

Perth is one of Australia’s fastest growing cities and the current economic growth pattern indicates this trend will continue (WAPC & DPI 2004).

The projected total population of Perth and Peel for 2031 will be some 2.22 million, an increase of 52% over the 2001 population (WAPC & DPI 2004).

2.3.3 Urban sprawl & Related Traffic Issues

At present, urban development in Perth stretches in a north south corridor from Butler in the north to Mandurah in the south. The beach provides the western boundary and the Darling Scarp forms the eastern boundary.

Perth’s long hot summers and the attraction of living by the beach, combined with the appeal of large low-density residential homes have contributed to Perth becoming a sprawling city. Problems associated with urban sprawl include:

- Extensive vegetation clearing for new subdivisions,
- Extensive infrastructure and facilities required (i.e. roads, schools, etc),
- Limited access to current public transport routes,
- People travelling greater distances to satisfy work and social requirements,
- Increased vehicle emissions, road congestion and traffic delays, and
- High dependence on motor vehicles.

On the basis of the 2.22 million Perth population by 2031, an estimated 375,000 additional new homes will be required in the Perth and Peel area (WAPC & DPI 2004). It is therefore essential that sustainable urban planning be executed to minimise further problems associated with expanding low-density suburbs already seen in the Perth metropolitan area.
2.4 MOTOR VEHICLES

Cars have been blamed for many of the detrimental environmental impacts that plague modern cities throughout the world. As shown in Table 1, expectations were definitely high when the motor vehicle was first invented:

<table>
<thead>
<tr>
<th>EXPECTED BENEFITS OF THE AUTOMOBILE</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Safer than a horse because of better control and braking</td>
</tr>
<tr>
<td>- Offers a means of cheap mass transit</td>
</tr>
<tr>
<td>- Insusceptible to weather conditions and fatigue</td>
</tr>
<tr>
<td>- Should relieve traffic congestion on city streets</td>
</tr>
<tr>
<td>- Should reduce city noise</td>
</tr>
<tr>
<td>- Permit movement to suburbia</td>
</tr>
</tbody>
</table>

*Table 1: Early 20th-century expectations for the Automobile (Rubin 2001)*

2.4.1 Car Dependence

Perth is one of the most car-dominated cities in the world (Siddique 2004) with Western Australia having the highest rate of vehicle ownership in Australia with 749 motor vehicles on register per 1000 people in 2004 (ABS 2004).

In 1995 Perth was ranked (in the world): (WAPC & DPI 2004)
- Third highest in road infrastructure length per capita,
- Fourth highest in car ownership, and
- Sixth highest in CBD parking spaces per job.

Car dependence is high with approximately 80% of the Perth population travelling to work or study in a private motor vehicle as driver or passenger (Parker 2004; WAPC & DPI 2004). If current trends of outward urban growth continue, this would increase the total distance of car travel from 23 million kilometres on a typical weekday in 1996 to almost 44 million kilometres by 2031 (DPI 2003a).

Vulnerability to changes in oil supply, rising greenhouse gas and precursor smog emissions from the transport sector, declining physical activity levels in the population and the financial burden of private motorised transport are compelling grounds for reducing the need to travel and shifting a greater share of trips from cars to other modes.
2.4.2 Emissions
According to the 1998/1999 emissions inventory for the Perth airshed, motor vehicles contributed 81% of the carbon monoxide (CO), 42% of the nitrogen oxides (NO\textsubscript{X}) and 32% of total volatile organic compounds (VOCs) (DEP 2002). A similar extent of contribution from motor vehicles has been observed in other Australian urban airsheds (Elsom 2004).

2.4.3 Incomplete Combustion
Incomplete combustion occurs when there is insufficient air to combust all the fuel in an engine cylinder, or when there is insufficient time or inadequate temperature to complete the combustion (Rubin 2001). Due to the pursuit of high power and high acceleration rates, car engines are in effect designed for incomplete combustion of fuels (Griffith University 2001).

When there is lack of air in the combustion process, thermal decomposition (pyrolysis) can set in. This decomposition process leads to the formation of new hydrocarbons, not originally contained in the fuel via the separation of hydrogen atoms (Baumbach 1996). This is also how a number of aromatic hydrocarbons (i.e. benzene, toluene, xylenes) are formed.

2.4.4 Aromatic Hydrocarbons
Aromatic hydrocarbons represent a major component of motor vehicle exhaust emissions (Jenkin et al. 2003). The six main groups of aromatic hydrocarbons found in vehicle exhaust emissions are benzene, toluene, xylenes, ethyl-toluene, ethyl-benzenes and tri-methyl benzenes. This was determined from analysis of the summary table (Appendix A) of annual emissions of reactive VOC species from the Perth motor vehicle fleet estimated for the 1998/1999-inventory year.

By virtue of their generally high reactivity and emission rate, the oxidation of aromatic hydrocarbons is believed to make a substantial contribution to the formation of ozone (Jenkin et al. 2003).
2.5 OZONE FORMATION POTENTIALS OF INDIVIDUAL VOCs

Researchers are continuously seeking better ways to identify the ozone formation potential of different species in order to devise more effective environmental regulations and control technologies (Rubin 2001). A number of methods (discussed below) have been developed to determine the potential ozone generation of individual VOCs:

2.5.1 The Carbon Mass Approach

This technique assumes that larger molecules are more reactive than smaller ones and focuses principally on the mass of carbon emitted. The advantage of this method is that it is simple and straightforward as only the total carbon emissions for each VOC needs to be compared.

There are problems with this simplistic method. It is well known that individual VOC compounds react at differing rates in the atmosphere (Saunders et al. 2003). Some VOCs are major players in the ozone formation process whereas other VOCs only participate marginally. Thus the carbon mass-based approach becomes flawed when significant efforts are made to reduce VOC emissions based purely on carbon mass. Reducing emissions of larger VOC species (not necessarily the most reactive VOC species), will have minimal impact on the net change in ozone generation.

2.5.2 The Reactive Organic Gas Approach

To incorporate the differences in chemical reactivity, two categories of VOCs were defined for regulatory purposes: unreactive and reactive species. Reactive species (referred to as reactive organic gases) are the compounds most responsible for ozone formation. In contrast, compounds which only react and contribute very slowly to ozone formation are considered to be unreactive species. Determining a classification system of VOCs into reactive and non-reactive was not easy.

In the mid-1980s the US Environmental Protection Authority decided to consider the reactivity of ethane ($\text{C}_2\text{H}_6$) with the $`\text{OH}$ radical as the dividing line between reactive and unreactive species (Rubin 2001). Therefore all VOCs that react with the $`\text{OH}$ radical more slowly than ethane were considered unreactive whilst all others were considered reactive organic gases.
Although this grouping into two categories was an improvement over the earlier carbon-based approach, more refined approaches were subsequently proposed.

2.5.3 A Chemical Reactivity Approach

A better way of comparing the ozone-forming potential of different hydrocarbons was to develop a reactivity scale.

The first such scale proposed (and used by air pollution control agencies) was based on the rate constant $k_{OH}$ for reactions with the OH radical (Rubin 2001). The advantage of the $k_{OH}$ scale is its simplicity; the reaction constants are known and do not depend on the geographic area of concern.

The disadvantage of this scale is that it considers only the reaction rate of the first step of the oxidation process of VOCs in the atmosphere. The remaining chemical reactions that lead to the conversion of NO to NO$_2$ and the formation of ozone are neglected.

2.5.4 Photochemical Ozone Creation Potentials (POCPs)

In an effort to account for the overall chemistry of ozone formation, a more useful definition of VOC reactivity is the *photochemical ozone creation potential* (POCP).

POCPs are not fundamental, geophysical quantities but are derived quantities (Derwent et al. 1996). The POCP value of a given compound depends on quantities such as rate coefficients and dry deposition velocities along with chemical properties of the urban atmosphere of concern (i.e. the VOC/NO$_X$ ratio, amounts and chemical composition of other VOCs that are present, etc).

POCP values are defined relative to a value of 100 for ethene, and represent the quantity of ozone formed from unit mass emission of a given VOC, relative to that from emission of an identical mass of ethene (Jenkin et al. 2003).
3. METHODS

3.1 EXPLICIT PERTH AIRSHED TROPOSPHERIC PHOTOCHEMICAL MODEL

3.1.1 Overview
Computer simulation is required to model the incredibly complicated system of an airshed. The relationship between peak smog levels and precursor NO$_X$ and VOC emissions defies simple analysis and thus computer modelling is required to best approximate photochemical smog production.

A highly detailed photochemical model to simulate the development of ozone and other photo-oxidants in the Perth airshed has been developed using data from the PPSS. The mathematical model simulates the tropospheric degradation and resultant secondary pollutant formation from emitted NO$_X$ and VOCs. The overall rate of these reactions combined with the concentration of various chemical species determines the rate and magnitude of predicted ozone concentrations.

The model is based upon local meteorology and emission conditions that are known to give rise to elevated ozone observations. The air parcel to encompass the regions emissions extends horizontally to the specified emitting area and to the top of the time-dependent boundary layer of the Perth airshed. The depth of the boundary layer starts at 300 metres at 6.00am and rises at a constant rate of increase throughout the morning to reach a height of 1800 metres by 2.00pm. Solar declination and latitude are set at –19.60 and –31.95026° respectively, appropriate for average summer time conditions in Perth (Saunders & Ma 2003).

3.1.2 Box Model
A photochemical box model features a single variable-volume reacting cell. This model is most appropriate for use with light winds, so that most of the emissions will remain in the cell and react, rather than being rapidly transported through the downwind side of the cell (Boubel et al. 1994).

A photochemical box model is therefore ideal for modelling peak ozone concentrations in the Perth airshed as maximum readings correspond with both light north easterly morning winds and light afternoon sea breezes.
Due to the isolation of Perth city, there are no major pollutant sources nearby that could potentially be blown into the Perth airshed region; this being a further reason why the photochemical box model is appropriate for modelling ozone concentrations within the Perth airshed (Noonan 1999).

3.1.3 Facsimile© Version 4

Facsimile© software provides a powerful means of solving differential equations encountered in scientific and engineering problems. It uses robust, reliable numerical techniques that are efficient for both small and large problems (MCPA Software 2004). Ordinary differential equations, chemical reactions and other boundary conditions are expressed in simple terms to Facsimile© by means of a special high-level programming language. Facsimile© is designed to solve stiff differential equations using a variable order Gear’s method (Saunders & Ma 2003).

Accurate simulation of the photochemical smog processes (i.e. complex non-linear reactions of NO\textsubscript{X} and VOCs) requires numerical solution of large systems of chemical equations (Noonan 1999). Facsimile© has proven to be one of the most adaptable software packages for dealing with large systems of simultaneously occurring complex chemical equations.

The chemical development of the species in the air parcel is described by a series of differential equations (Saunders & Ma 2003) in the form:

\[
\frac{dC_i}{dt} = P - L_i C_i - \frac{V_i C_i}{h} + \frac{E_i}{h} - \frac{(C_i - B_i)}{h.dh}
\]

Where:
- \(C_i\) = Species concentration
- \(t\) = Time
- \(P\) = Instantaneous production from photochemistry
- \(L\) = Instantaneous loss rate from photochemistry
- \(V\) = Species dependent dry deposition velocity
- \(h\) = Time-dependent boundary layer depth
- \(E\) = Local emission rate from airshed sources
- \(B_i\) = Background concentration
As the boundary layer depth expands, air is entrained from the free troposphere above. This process is described by the following part of the differential equation:

\[ (C_i - B_i) \frac{dh}{h \, dt} \]

To solve these differential equations, we first need to describe the chemical transformations taking place for all the relevant VOCs.

### 3.1.4 Master Chemical Mechanism (MCM)

The MCM was developed as a research tool for modelling processes such as the formation of photochemical smog. The MCM provides an explicit description of the degradation chemistry (see example - Figure 8) for individual VOC species and the associated contribution to ozone formation (University of Leeds 2005). The MCM can be accessed via the University of Leeds website (http://mcm.leeds.ac.uk/MCM).

Figure 8: Schematic of Toluene Oxidation Mechanism

MCM Version 3.1

It is well established that the degradation of each emitted VOC occurs by a unique mechanism (because of differences in reactivity and structure), such that the relative contributions of VOC to the formation of ozone and other secondary pollutants varies from one compound to another (Saunders et al. 2003). These mechanisms must be reviewed and maintained in line with current literature. Version 3.1 of the MCM is the most up-to-date description of VOC degradation chemistry (Saunders et al. 2003).
The representation of mechanisms describing the degradation of aromatic hydrocarbons in air quality models has long been hampered by an incomplete knowledge of the detailed chemistry (Jenkin et al. 2003). MCM Version 3.1 has made significant improvements to the knowledge of aromatic degradation chemistry with an additional 176 species and 825 new reactions added to the MCM database. The updated MCM Version 3.1 has a total of 13,569 chemical reactions and more than 4,600 chemical species. Version 3.1 degradation chemistry (inclusive of extensive aromatic chemistry) has been updated within the Perth Airshed Model.

### 3.1.5 Adjustment of Temperature Profile

Temperature has a large effect on all chemical reactions. With over 13,500 chemical reactions being processed within the airshed model, the temperature profile is considered to be an important parameter within the Perth Airshed Model.

As can be seen in Figure 9, the profile used in the original model (pink line) is a simplified step-function and is non-representational of a hot summers day in Perth. Data was collected from the Bureau of Meteorology for a 24-hour period in March 2005 and can be seen represented by the blue line in Figure 9.

![24-HOUR TEMPERATURE PROFILE (°C)](image)

**Figure 9:** Comparison of the updated temperature profile to the one used in the original model (Bureau of Meteorology 2005)
3.1.6 Adjustment of Emitting Area

The original model used an emitting area of 2,800 square kilometres. This represents approximately 35% of the total study region (represented in Figure 4). After reviewing the study region, a more accurate estimate of the emitting area was determined to be 6,435 square kilometres (~70% of the study region). This is the equivalent area to the total landmass within the study region.

3.1.7 24-Hour Emission Profiles

A summary of estimated hourly emissions from the Perth motor vehicle fleet for the 1998/1999-inventory period was determined and is given in Appendix B (DEP 2002). The hourly breakdown was determined by analysing vehicle fleet data combined with activity data. Table 2 gives the hourly emissions over a 24-hour period as a percentage of the entire day’s emissions:

<table>
<thead>
<tr>
<th>Hour of the Day</th>
<th>% Daily Emission</th>
<th>Hour of the Day</th>
<th>% Daily Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.00 – 1.00am</td>
<td>0.5%</td>
<td>12.00 – 1.00pm</td>
<td>5.7%</td>
</tr>
<tr>
<td>1.00 – 2.00am</td>
<td>0.3%</td>
<td>1.00 – 2.00pm</td>
<td>5.7%</td>
</tr>
<tr>
<td>2.00 – 3.00am</td>
<td>0.2%</td>
<td>2.00 – 3.00pm</td>
<td>6.4%</td>
</tr>
<tr>
<td>3.00 – 4.00am</td>
<td>0.3%</td>
<td>3.00 – 4.00pm</td>
<td>7.6%</td>
</tr>
<tr>
<td>4.00 – 5.00am</td>
<td>0.6%</td>
<td>4.00 – 5.00pm</td>
<td>8.2%</td>
</tr>
<tr>
<td>5.00 – 6.00am</td>
<td>2.0%</td>
<td>5.00 – 6.00pm</td>
<td>7.7%</td>
</tr>
<tr>
<td>6.00 – 7.00am</td>
<td>5.7%</td>
<td>6.00 – 7.00pm</td>
<td>5.4%</td>
</tr>
<tr>
<td>7.00 – 8.00am</td>
<td>8.1%</td>
<td>7.00 – 8.00pm</td>
<td>3.5%</td>
</tr>
<tr>
<td>8.00 – 9.00am</td>
<td>7.2%</td>
<td>8.00 – 9.00pm</td>
<td>2.6%</td>
</tr>
<tr>
<td>9.00 – 10.00am</td>
<td>5.7%</td>
<td>9.00 – 10.00am</td>
<td>2.4%</td>
</tr>
<tr>
<td>10.00 – 11.00am</td>
<td>5.5%</td>
<td>10.00 – 11.00pm</td>
<td>1.9%</td>
</tr>
<tr>
<td>11.00 – 12.00pm</td>
<td>5.6%</td>
<td>11.00 – 12.00am</td>
<td>1.2%</td>
</tr>
<tr>
<td><strong>WHOLE DAY 100%</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2:** Estimated hourly emissions of motor vehicle emissions

The motor vehicle emissions category was the only inventory, which had this hourly breakdown of estimated emissions data. Therefore the other three categories were assumed to be constant throughout the day.
To calculate the total estimated hourly emissions for all four categories, the combined daily emissions from the other three categories (industrial, area-based and biogenic) were divided equally over the 24-hour period. The hourly motor vehicle emissions were calculated as per Table 2. These values were combined to derive the estimated hourly emissions for the particular emission type (i.e. NO\textsubscript{X}).

This methodology was also applied to the 1992/1993-inventory period as the motor vehicle emissions were expected to follow a similar 24-hour profile.

**Code - Emission Parameters**

The Facsimile\textsuperscript{©} programming language requires the hourly emissions to be read in as “millimoles per square metre per day”. Table 3 shows the required calculations to convert “Tonnes per Year” to “Millimoles per m\textsuperscript{2} per Day”

<table>
<thead>
<tr>
<th>CALCULATION TO CONVERT TO REQUIRED UNIT</th>
<th>REQUIRED UNIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiply by 1000 &amp; Divide by 365</td>
<td>Tonnes per Year</td>
</tr>
<tr>
<td>Divide by 6.435 x 10\textsuperscript{9} m\textsuperscript{2} ( Emitting Area)</td>
<td>Kilograms per Day</td>
</tr>
<tr>
<td>Multiply by 1000</td>
<td>Kilograms per m\textsuperscript{2} per Day</td>
</tr>
<tr>
<td>Divide by molecular weight of emission type</td>
<td>Grams per m\textsuperscript{2} per Day</td>
</tr>
<tr>
<td>Multiply by 1000</td>
<td>Moles per m\textsuperscript{2} per Day</td>
</tr>
<tr>
<td>Multiply by 1000</td>
<td>Millimoles per m\textsuperscript{2} per Day</td>
</tr>
</tbody>
</table>

**Table 3:** Calculation method to convert “Tonnes per Year” to “Millimoles per m\textsuperscript{2} per Day”

### 3.1.8 Comparison of NO\textsubscript{X} Emission Profiles

Total NO\textsubscript{X} emissions for the 1998/1999 reporting year were 70,253 tonnes (or 192,474 kilograms per day). The motor vehicle category accounted for 41% of these emissions. The yellow line in Figure 10 represents the simplistic step-function used in the original model. The blue line represents the 1998/1999 NO\textsubscript{X} 24-hour emission profile and the pink line represents the 1992/1993 NO\textsubscript{X} 24-hour emission profile.
The NO\textsubscript{x} emission profiles for the 1992/1993 and 1998/1999 inventories appear to be realistic and representational of the 24-hour period as they accurately capture the two peaks from rush-hour traffic emissions.

![HOURLY NO\textsubscript{x} EMISSIONS](image)

**Figure 10:** The updated 24-hour NO\textsubscript{x} emission profile for the 1998/1999 and 1992/1993 inventory compared to the step-function profile used in the original model

### 3.1.9 Comparison of VOC Emission Profiles

Total VOC emissions for the 1998/1999 reporting year were 69,661 tonnes (or 190,852 kilograms per day). The motor vehicle category accounted for 32% of these emissions.

The yellow line in Figure 11 represents the simplistic step-function used in the original model. The blue line represents the 1998/1999 VOC 24-hour emission profile and the pink line represents the 1992/1993 VOC 24-hour emission profile.

Again we see the more realistic VOC emission profiles for the 1992/1993 and 1998/1999 inventories, capturing the two peaks from rush-hour traffic emissions.
Figure 11: The updated 24-hour VOC emission profile for the 1998/1999 and 1992/1993 inventory compared to the step-function profile used in the original model

3.1.10 Comparison of CO Emission Profiles

Total CO emissions for the 1998/1999 reporting year were 283,336 tonnes (or 776,263 kilograms per day). The motor vehicle category accounted for 81% of these emissions.

The yellow line in Figure 12 represents the simplistic step-function used in the original model, which massively underestimated actual CO emissions. The blue line represents the 1998/1999 CO 24-hour emission profile and the pink line represents the 1992/1993 CO 24-hour emission profile.

The VOC emission profiles for the 1992/1993 and 1998/1999 inventories are very similar but differ significantly from the profile used in the original model.
3.1.11 Comparison of BIOGENIC Emission Profiles

Isoprene (ISO) is the major hydrocarbon emitted by vegetation and is very reactive with the hydroxyl radical (‘OH) and with ozone (O₃) (AMS 2005). Biogenic emissions of isoprene are strongly dependent on leaf temperature and availability of sunlight (DEP 2002).

The approach taken in estimating biogenic emissions was to relate them to vegetation density using satellite photographs (DEP & Western Power 1996). The vegetation species distribution for the Perth region was derived using natural vegetation maps. Published canopy emission rates were then used to derive biogenic emission estimates for the region. There are concerns over the quality of data available to define biogenic and natural emissions and the accuracy of the estimation methodology (DEP & Western Power 1996)(DEP 2002).

As can be seen in Figure 13, the original estimates of ISO emissions (made in the PPSS) for the Perth region were based on a worst-case scenario (DEP & Western Power 1996) and are represented by the blue line. The revised estimated emissions for both the 1992/1993 and 1998/1999 inventories were assumed to be the same at 16,000 tonnes per year (or 43,835 kilograms per day) as represented by the pink line.
Figure 13: The updated 24-hour ISO emission profile for the 1992/1993 and 1998/1999 inventory (same), compared to the profile used in the original model

3.1.12 Updating of Complex Rate Coefficients

The International Union of Pure and Applied Chemistry (IUPAC) website (located at http://www.iupac-kinetic.ch.cam.ac.uk/) hosts an interactive database with a search facility and implemented hyperlinks on gas kinetic data evaluation for atmospheric chemistry (IUPAC 2005). Complex rate coefficients have been updated to 2005 recommendations within the Perth Airshed Model as shown below in Table 4:

Table 4 – Example of Facsimile© Programming Language showing updated Complex Rate Coefficients for Reaction $N_2O_5 = NO_2 + NO_3$

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{MT04}$</td>
<td>$(K_{40} K_{4I}) Fa_4 / (K_{40} + K_{4I})$</td>
</tr>
<tr>
<td>$K_{40}$</td>
<td>$1.30D-03*(TEMP/300)^{-3.5}*\exp(-11000/TEMP)$</td>
</tr>
<tr>
<td>$K_{4I}$</td>
<td>$9.70D+14*(TEMP/300)^{0.1}*\exp(-11080/TEMP)$</td>
</tr>
<tr>
<td>$KR4$</td>
<td>$K_{40} / K_{4I}$</td>
</tr>
<tr>
<td>$FC4$</td>
<td>0.35</td>
</tr>
<tr>
<td>$N_b$</td>
<td>$(0.75-1.27*\log_{10}(FC4))$</td>
</tr>
<tr>
<td>$Fa_4$</td>
<td>$10^{((\log_{10}(FC4)/1+(\log_{10}(KR4)/N_b)**2))}$</td>
</tr>
<tr>
<td>$K_{MT04}$</td>
<td>$(K_{40} K_{4I}) Fa_4 / (K_{40} + K_{4I})$</td>
</tr>
</tbody>
</table>
3.1.13 Calculation of Photochemical Indicators

Determining whether individual air pollution events are dominated by NO$_X$-sensitive or VOC-sensitive chemistry can be a difficult and lengthy modelling task.

Milford et al. (1994) and Sillman (1995) developed an alternative approach for evaluating NO$_X$-VOC sensitivity. They found that model predictions for NO$_X$-VOC sensitivity were linked to simulated afternoon concentrations of a number of key species (Sillman et al. 1997).

Milford et al. (1994) demonstrated that VOC-sensitive ozone in models was associated with afternoon values of total reactive nitrogen (NO$_Y$) above a certain threshold concentration. NO$_X$-sensitive ozone was associated with lower afternoon concentrations of total reactive nitrogen (NO$_Y$).

Sillman (1995) extended the work of Milford et al. (1994) further to include other species and species ratios including:

- $\text{O}_3 / \text{NO}_Y$ (where NO$_Y$ = NO + NO$_2$ + HNO$_3$ + Total PAN + NA),
- $\text{O}_3 / \text{NO}_Z$ (where NO$_Z$ = HNO$_3$ + Total PAN + NA), and
- $\text{H}_2\text{O}_2 / \text{HNO}_3$

To determine whether the Perth airshed model was either VOC or NO$_X$ sensitive, the ratio $\text{O}_3 / \text{NO}_Z$ was applied. This involved determining the afternoon concentrations of ozone ($\text{O}_3$) along with the combined afternoon concentrations of nitric acid, total PAN species and nitrate aerosols.

3.1.14 Future Scenarios

Three unique scenarios were developed to forecast changes in maximum ozone concentrations in the Perth airshed for 10 years time. The corresponding emissions approximated for the three scenarios are summarised in Table 5:
From comparison of the 1992/1993 and 1998/1999 inventories, total NO\textsubscript{X} emissions increased by approximately 30%. Projecting this trend forward (i.e. 30% increase over five years), we would expect to see NO\textsubscript{X} emissions increase by approximately 60% in the next 10 years.

Total VOC emissions decreased by approximately 18% between 1992/1993 and 1998/1999. Following this trend, VOC emissions in Scenario 1 are expected to remain reasonably steady and therefore no change to the VOC emissions were made.

In addition to altering the mass of emissions, changes were also made to the actual composition of the VOC emissions. As aromatic hydrocarbons represent a significant component of motor vehicle exhaust emissions, and as motor vehicle emissions are expected to increase due to increased population and increased kilometres travelled, we can expect to see an increase in the aromatic component of VOC emissions.

The 1992/1993 and 1998/1999 aromatic composition of VOC emissions within the *Perth Airshed Model* is approximately 16%. For Scenario #1, this composition has been increased by approximately 9% to a total of 25% aromatic composition.

---

**Table 5: Summary of the Change in Emissions for the 3 Forecasted Scenarios**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Change in Mass of NO\textsubscript{X} Emissions</th>
<th>Change in Mass of VOC Emissions</th>
<th>Aromatic Component of VOC Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>60% ↑</td>
<td>NO CHANGE</td>
<td>25%</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>400% ↑</td>
<td>20% ↑</td>
<td>40%</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>20% ↓</td>
<td>50% ↑</td>
<td>40%</td>
</tr>
</tbody>
</table>
Scenario #2: Dramatic Increase of NO\textsubscript{\textsuperscript{X}} Emissions

Most urban environments are saturated with VOCs (Rubin 2001) and therefore any small changes made to total VOC emissions have negligible effect on total ozone generation. For this reason, the majority of urban airsheds around the world are NO\textsubscript{\textsuperscript{X}}-sensitive and therefore we anticipate that the Perth airshed ozone generation will be more responsive to increased NO\textsubscript{\textsuperscript{X}} emissions rather than increased VOC emissions. Scenario #2 represents a worst-case scenario for the Perth airshed with a massive 400% increase in NO\textsubscript{\textsuperscript{X}} emissions.

The mass of VOC emissions have also been increased by 20% and the aromatic composition of total VOC emissions have been increased further from Scenario #1 to 40%. The VOC emissions breakdown showing the different aromatic compositions (i.e. 16%, 25% and 40%) can be viewed in Appendix C.

Scenario #3: NO\textsubscript{\textsuperscript{X}} Policy Implemented

This scenario represents the effects of reducing the total mass of NO\textsubscript{\textsuperscript{X}} emissions by 20% by implementing some form of NO\textsubscript{\textsuperscript{X}} policy or control strategy.

The mass of VOC emissions in Scenario #3 has been increased by 50%. The rationale for increasing VOC emissions by this extent stems from the idea that adhering strict policy on one substance (i.e. NO\textsubscript{\textsuperscript{X}}) will possibly enhance the use of other substances (i.e. VOCs) (Boubel et al. 1994). The composition of aromatic VOC emissions is 40%, as per Scenario #2

3.1.15 Removal Analysis

To determine which aromatic VOCs have the largest impact on ozone generation within the Perth airshed, the six main groups of aromatic hydrocarbons found in vehicle exhausts (i.e. toluene, benzene, xylenes, ethyl toluene, ethyl benzenes and trimethyl benzenes) were removed one at a time from the *Perth Airshed Model* VOC emissions.
The complete removal of an individual VOC from an airshed inventory is an innovative and realistic way of assessing the ozone formation potential of a species. For example, if an aromatic compound was completely banned from fuels, we would expect to see vehicle exhaust emissions contain substantially less (or possibly zero) of that particular compound.

The removal analysis (i.e. individual removal of six main aromatic compounds) was carried out on both Scenario #2 and Scenario #3 to see the changes (if any) in ozone generation throughout the day.
4. RESULTS

4.1 OZONE CONCENTRATION PROFILES

Modelling results are shown for the 1992/1993 and 1998/1999 emission inventories.

4.1.1 1992/1993 Ozone Profile
- Maximum Ozone Concentration: 141ppb
- \( \text{O}_3/\text{NO}_2 \) Ratio: 23.6

Figure 14: Ozone concentration profile for 1992/1993 emissions inventory

4.1.2 1998/1999 Ozone Profile
- Maximum Ozone Concentration: 148ppb
- \( \text{O}_3/\text{NO}_2 \) Ratio: 21.1

Figure 15: Ozone concentration profile for 1998/1999 emissions inventory
Modelling results are shown below for the three predicted scenarios.

4.1.3 Scenario #1 Ozone Profile

- Maximum Ozone Concentration: 165ppb
- $\text{O}_3/\text{NO}_2$ Ratio: 16.8

**Figure 16**: Ozone concentration profile for Scenario #1

4.1.4 Scenario #2 Ozone Profile

- Maximum Ozone Concentration: 209ppb
- $\text{O}_3/\text{NO}_2$ Ratio: 8.5

**Figure 17**: Ozone concentration profile for Scenario #2
4.1.5 Scenario #3 Ozone Profile

- Maximum Ozone Concentration: 142ppb
- \(O_3/NO_2\) Ratio: 23.4

![Graph showing Ozone concentration profile for Scenario #3](image)

**Figure 18:** Ozone concentration profile for Scenario #3

**REMOVAL ANALYSIS**

The following figures (#19-30) show the deviation in ozone concentration throughout the day (from either Scenario #2 or Scenario #3) when an aromatic species is completely removed from the airshed VOC emissions.

A decrease in ppb corresponds to an overall decrease in ozone generation throughout the day due to removal of that particular aromatic species.

An increase in ppb corresponds to an overall increase in ozone generation throughout the day due to removal of that particular aromatic species.
4.2 REMOVAL ANALYSIS – TOLUENE

4.2.1 Removal of Toluene from Scenario #2

Deviation from Scenario #2 Profile: $\downarrow 13 \text{ ppb O}_3$

![Figure 19: Deviation from Scenario #2 Ozone Concentration Profile by removal of Toluene from airshed emissions](image)

4.2.2 Removal of Toluene from Scenario #3

Deviation from Scenario #3 Profile: $\uparrow 2 \text{ ppb O}_3$

![Figure 20: Deviation from Scenario #3 Ozone Concentration Profile by removal of Toluene from airshed emissions](image)
4.3 REMOVAL ANALYSIS – BENZENE

4.3.1 Removal of Benzene from Scenario #2

- Deviation from Scenario #2 Profile: ↑ 0.5 ppb O₃

Figure 21: Deviation from Scenario #2 Ozone Concentration Profile by removal of Benzene from airshed emissions

4.3.2 Removal of Benzene from Scenario #3

- Deviation from Scenario #3 Profile: ↑ 1.5 ppb O₃

Figure 22: Deviation from Scenario #3 Ozone Concentration Profile by removal of Benzene from airshed emissions
4.4 REMOVAL ANALYSIS – ETHYL BENZENES

4.4.1 Removal of Ethyl benzenes from Scenario #2

- Deviation from Scenario #2 Profile: $\downarrow 2$ ppb $O_3$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure23}
\caption{Deviation from Scenario #2 Ozone Concentration Profile by removal of Ethyl benzenes from airshed emissions}
\end{figure}

4.4.2 Removal of Ethyl benzenes from Scenario #3

- Deviation from Scenario #3 Profile: $\uparrow 1$ ppb $O_3$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure24}
\caption{Deviation from Scenario #3 Ozone Concentration Profile by removal of Ethyl benzenes from airshed emissions}
\end{figure}
4.5 REMOVAL ANALYSIS – XYLENES

4.5.1 Removal of Xylenes from Scenario #2

Deviation from Scenario #2 Profile: ↓ 22 ppb $O_3$

![Graph showing deviation from Scenario #2 Ozone Concentration Profile](image)

**Figure 25:** Deviation from Scenario #2 Ozone Concentration Profile by removal of Xylenes from airshed emissions

4.5.2 Removal of Xylenes from Scenario #3

Deviation from Scenario #3 Profile: ↓ 3.5 ppb $O_3$

![Graph showing deviation from Scenario #3 Ozone Concentration Profile](image)

**Figure 26:** Deviation from Scenario #3 Ozone Concentration Profile by removal of Xylenes from airshed emissions
4.6 REMOVAL ANALYSIS – TRI-METHYL BENZENES

4.6.1 Removal of Tri-methyl benzenes from Scenario #2

Deviation from Scenario #2 Profile: ↓ 30 ppb O₃

![Figure 27: Deviation from Scenario #2 Ozone Concentration Profile by removal of Tri-methyl benzenes from airshed emissions](image)

4.6.2 Removal of Tri-methyl benzenes from Scenario #3

Deviation from Scenario #3 Profile: ↓ 13ppb O₃

![Figure 28: Deviation from Scenario #3 Ozone Concentration Profile by removal of Tri-methyl benzenes from airshed emissions](image)
4.7 REMOVAL ANALYSIS – ETHYL TOLUENE

4.7.1 Removal of Ethyl toluene from Scenario #2

Deviation from Scenario #2 Profile: \( \downarrow 1 \text{ ppb O}_3 \)

![Figure 29: Deviation from Scenario #2 Ozone Concentration Profile by removal of Ethyl toluene from airshed emissions](image)

4.7.2 Removal of Ethyl toluene from Scenario #3

Deviation from Scenario #3 Profile: \( \uparrow 0.5 \text{ ppb O}_3 \)

![Figure 30: Deviation from Scenario #3 Ozone Concentration Profile by removal of Ethyl toluene from airshed emissions](image)
5. DISCUSSION

5.1 DISCUSSION OF MODELLING RESULTS

5.1.1 1992/1993 vs. 1998/1999 Ozone Profile

Noteworthy discrepancies between the 1992/1993 and 1998/1999 emission inventories include an increase in NO\textsubscript{X} emissions (~30%) and decrease in VOC emissions (~18%). This results in an increase of maximum peak ozone concentration from 141ppb to 148ppb as can be seen in Figure 31.

During the PPSS monitoring (1992-1995), there was an average of 10 days per year where peak hourly ozone concentrations exceeded the NHMRC goal of 80 ppb. Although an increase of 7 ppb is not considered massive, if ozone concentrations continue to increase, the number days where peak hourly ozone concentrations exceed 80 ppb will without doubt increase.

![Figure 31: Comparison of 1992/1993 and 1998/1999 ozone concentration profiles](image)

Emission inventories remain one of the major uncertainties of modelling efforts. For example, it is very difficult to derive conclusions about real changes in emissions by comparing the 1992/1993 and 1998/1999 emission inventories.
Variation in emissions may be attributed to improvements in methodology and data quality, rather than actual changes in emissions. For instance, more industrial facilities were considered and additional area-based source categories were included in the 1998/1999 inventory.

As can be seen in Appendix D, total industrial emissions increased by 32 tonnes over these reporting periods. If more industrial facilities were included, this could possibly mean that the industrial sources that were used in both inventories have dropped their emission rates by considerable amounts.

From the 1992/1993 to the 1998/1999 emissions inventory, the $O_3/NO_x$ ratio dropped from 23.6 down to 21.1. Whilst both of these reporting years are obviously NOX-limited (due to the high ratio greater than 10), the lower this ratio becomes, the more VOC-limited the system becomes. With reference to Figure 32, an increase in NOX emissions (represented by the red triangles) and a decrease in VOC emissions (represented by the star shapes), shows that the system becomes less saturated with VOC emissions.

![Figure 32: Schematic example of the VOC/NOX ratio change from 1992/1993 to 1998/1999](image)

The original *Perth Airshed Model* created by Saunders and Ma in 2003 has been modified in many ways to create a more realistic and enhanced representation of the Perth airshed. The original model used 1992/1993 emission values from the original PPSS report (Cope & Ischtwan 1995). Some of these values vary significantly from 1992/1993 emission figures released by the Department of Environment in the 2002 Technical Report (DEP 2002).
Another change made to the *Perth Airshed Model* was increasing the size of the emitting area. This change in effect, causes the emission concentrations to become diluted and has the potential to have a large impact on maximum ozone concentrations generated with the airshed.

The results produced by the *Perth Airshed Model* are unable to be directly compared to “real” monitoring results from locations around Perth. The modelled results give an overall averaged concentration for the ozone produced within the airshed. Monitoring results are point concentrations from a specific location. Due to the nature of the model (i.e. box model), maximum point concentrations are unable to be determined.

### 5.1.2 Limitations of Box Model

The performance of photochemical models is evaluated by their ability to estimate the magnitude, time and location of occurrence of the secondary pollutant oxidant (ozone) (Boubel et al. 1994). The box model is capable of estimating magnitude and time, but fails to define the specific location of ozone within the entire airshed.

The box model is the simplest concept for the calculation of an air volume’s composition. The assumption necessary for modelling an atmosphere over an urban area with a box model is that the airshed behaves as a well-mixed box (i.e. mixing within the air parcel is assumed to be instantaneous and complete). Air movements induced by turbulent diffusion and wind flows inside the box are not taken into consideration.

A more sophisticated type of airshed model that can specify locations of maximum ozone concentration is the Langrangian Model. This model stems from the statistic diffusion theory which is based on the fact that air pollutants are always carried along with the average wind flow (by means of a certain distribution) (Noonan 1999). Although diffusion is statistically random, a class of distribution models can be directly derived (i.e. gaussian distribution) (Baumbach 1996).
The gaussian “plume” model presumes that emissions from a source travel directly downwind, dispersing in the horizontal and vertical directions, with concentration profiles following a gaussian distribution. The gaussian puff model is an enhancement of the traditional plume model and represents the emissions as a sequence of puffs released from the source, each puff dispersing in directions both across and along the current wind condition, as well as vertically.

These Langrangian models are capable of handling input of complicated meteorological conditions, including the effects of topography and near coastal variations of stability and mixing depth resulting in a more accurate model output (DoE 2005a).

5.1.3 Scenario #1 vs. Scenario #2 vs. Scenario #3

Figure 33 illustrates the divergence in expected ozone generation for the three predicted scenarios.

![10-Year Projections](image)

**Figure 33: Comparison of Ozone Concentration Profiles of Scenario #1, Scenario #2 and Scenario #3**
Many factors will determine which Scenario is most likely in Perth in ten years time, including:

- Motor vehicle use (including vehicle population and kilometres travelled),
- Emission standards (and monitoring of older vehicles),
- Fuel quality (and cost),
- Extent of urban sprawl, and
- Utilisation of public transport.

**Scenario 1:**
165ppb is the predicted peak ozone concentration likely if we continue to do things the way we are currently. This corresponds to an increase of 17 ppb and represents a concentration that is greater than double the NEPM ozone goal of 80 ppb. Since this prediction is an averaged concentration for the entire airshed, Perth could experience much more intense levels than this in susceptible areas.

**Scenario 2:**
209ppb is definitely a worst-case scenario prediction. This corresponds to a steep increase in the mass of NO\textsubscript{X} emissions emitted into the Perth airshed and results in a maximum ozone concentration almost three times the NEPM goal (80ppb).

The large increase in NO\textsubscript{X} emissions combined with the small increase (20%) in VOC emissions brings about an important change to the O\textsubscript{3}/NO\textsubscript{X} ratio. The ratio drops to 8.5 and this therefore means that the Scenario #2 system is VOC-limited.

**Scenario 3:**
An estimated maximum ozone concentration of 142 ppb is the most ideal outcome out of all three scenarios. This would actually reduce the maximum ozone concentration estimated for the 1998/1999 reporting year by 6ppb.

Scenario #3 decreases NO\textsubscript{X} emissions by 20%, but also increases VOC emissions by a substantial 50%. The O\textsubscript{3}/NO\textsubscript{X} ratio of 23.4 determines that the system is more NO\textsubscript{X}-limited than any of the other scenarios. This is the reason why the system is so responsive to the 20% decrease in NO\textsubscript{X} emissions.
5.1.4 Removal Analysis

Three separate outcomes were discovered when analysing the results of removing six individual aromatic compounds from Scenario #2 and Scenario #3;

1. Removal of the aromatic compound resulted in ozone concentration reduction in both Scenario #2 and Scenario #3,
2. Removal of the aromatic compound resulted in ozone concentration increasing in Scenario #3 and decreasing in Scenario #2, and
3. Removal of the aromatic compound resulted in ozone concentration increasing in both Scenario #2 and Scenario #3.

Case 1: Removal of Aromatic Compound = Reduction in Ozone Generation
Removal of the aromatic compounds Xylenes and Tri-methyl benzenes results in overall reductions of ozone in both VOC-sensitive Scenario 2 and NO\textsubscript{X}-sensitive Scenario 3. In both removals, the ozone is reduced more significantly in the VOC-limited Scenario 2. This can be expected by reference to the schematic below (Figure 36). If we were to remove a VOC (star-shape) from the left-hand system (NO\textsubscript{X}-limited), the system would remain saturated with VOCs and the change in ozone production would be insignificant. Removal of a VOC species from the right-hand system (VOC-limited) would reduce the number of potential reactions from occurring and consequently have a more substantial impact on ozone production.

Figure 36: Schematic of a NO\textsubscript{X}-limited system (LEFT) and a VOC-limited system (RIGHT)

Case 2: Removal of Aromatic Compound = Increase in ozone production in NO\textsubscript{X}-limited systems and decrease in ozone production in VOC-limited systems

Figure 37: Removal Analysis of Toluene
Comparison of Deviation from Scenario #2 and Scenario #3 Ozone Concentration Profiles
The importance of carrying out the removal analysis in both NO\textsubscript{X}-limited and VOC-limited systems is illustrated when analysing the removal of Toluene, Ethyl benzenes and Ethyl toluene.

In all three cases, removal of the aromatic species in the VOC-limited system has caused an overall reduction in ozone production throughout the day, whilst an overall increase in ozone production has been observed in the NO\textsubscript{X}-limited systems.
The analysis of both VOC-limited and NO$_X$-limited systems is important when determining which aromatic species contributes the most to ozone production. If analysis of only one system (i.e. VOC-limited) was carried out, the above results demonstrate that removal of Toluene, Ethyl benzenes and Ethyl toluene from the airshed would reduce overall ozone generation throughout the day and that therefore policy should restrict these emissions into the Perth airshed.

On the other hand, if we were to only look at the removal analysis from the NO$_X$-limited system, the results inform us that removal of Toluene, Ethyl benzenes and Ethyl toluene actually increase ozone generation throughout the day and therefore removal of these compounds is not imperative to reduce ozone concentrations.

This double set of results provide confirmation that choice of policy focus needs to be continually assessed as airshed emissions change over time.

Case 3: Removal of Aromatic compound = Increase in Ozone Generation

The removal of benzene from the total mass of VOC emissions reveals very interesting results. Both the NO$_X$-limited and VOC-limited systems actually increase (albeit slightly) the total amount of ozone generated throughout the day.
Further analysis would involve increasing benzene emissions to see whether this actually reduces the level of ozone created throughout the day. This would certainly not be a solution to reducing ozone concentrations as would ultimately end up with higher atmospheric concentrations of benzene (a known carcinogen (NSC 2005)).

Further analysis is required throughout the 13,000-plus intermediate reaction-steps of the model run to determine which reactions are causing the ozone concentration to increase throughout the day. It is suspected that remaining VOCs are adjusting due to a highly non-linear nature of the complex system and are able to give an enhanced ozone production, which otherwise would be taken up by the benzene reaction pathways.

5.1.5 Aromatic VOC Concentration Levels In Perth

The Department of Environment Protection (DEP) conducted a study of airborne VOCs in Perth from March 1997 to November 1998. The principal aim of the project was to assess Perth’s ambient air for VOC composition and concentration (DEP 1998). The DEP monitoring sites for this particular study are shown in Figure 41:

Figure 41: VOC monitoring sites (DEP 1998)
A total of 157 samples were taken and analysed during the course of the study with a total of 23 VOCs detected in air samples taken around Perth (DEP 1998).

Of the 23 VOCs detected, eight had higher than typical background level concentrations. Benzene, toluene and xylenes were the most abundant compounds at all the monitoring sites as shown in Figure 42:

![Figure 42: Average 24-hour VOC concentrations at monitoring sites (DEP 1998)](image)

Out of the eight VOC species with higher than typical background concentrations (as seen in Figure 42), only two of them (i.e. Freon-11 and Freon-12) are not emitted from motor vehicle exhaust systems.
<table>
<thead>
<tr>
<th>AROMATIC VOC SPECIES</th>
<th>% VOC Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>16%</td>
</tr>
<tr>
<td>Ethyl Benzenes</td>
<td>2%</td>
</tr>
<tr>
<td>Tri-methyl Benzenes</td>
<td>6%</td>
</tr>
<tr>
<td>Xylenes</td>
<td>9%</td>
</tr>
<tr>
<td>Benzene</td>
<td>5%</td>
</tr>
<tr>
<td>Ethyl Toluene</td>
<td>1%</td>
</tr>
</tbody>
</table>

Table 6: Summary of VOC Emission Percentage for Scenario #2 and Scenario #3

![Graph showing Total Change in Ozone Contribution](image)

Figure 43: Ozone Contribution of each Aromatic Compound

Out of the six aromatic species removed from Scenario #2 and Scenario #3, Toluene comprises the largest percentage of VOC emissions in terms of mass (i.e. 16%). The removal of Toluene would therefore have been expected to impact the most on ozone generation throughout the day. Figure 43 verifies this assumption to be incorrect as Tri-methyl benzenes and Xylenes appear to have the greatest impact on ozone contribution with a 30 ppb and 22 ppb decrease respectively. Tri-methyl benzenes comprised of only 6% of total VOC emissions and Xylenes comprised of 9%, both well below the 16% mass of Toluene. These results show the higher reactivity and higher ozone formation potential of these two aromatic compounds.

Figure 43 also illustrates how VOC-limited Scenario #2 is much more sensitive to the removal of aromatic species as compared to the NOX-limited Scenario #3.
5.2 POLICY

5.2.1 Western Australian Air Quality

All States and Territories have agreed to national air quality standards. These standards (called the “National Environmental Protection Measure for Ambient Air Quality” or Air NEPM) set limits on six pollutants, which must be met by 2008 (EDOWA 2003). These limits are shown below in Table 7:

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Averaging Time</th>
<th>Maximum Concentration</th>
<th>Allowed Exceedances (10 year goal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>8 hours</td>
<td>900 ppb</td>
<td>1 day a year</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>1 hour</td>
<td>120 ppb</td>
<td>1 day a year</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>30 ppb</td>
<td>0</td>
</tr>
<tr>
<td>Ozone</td>
<td>1 hour</td>
<td>100 ppb</td>
<td>1 day a year</td>
</tr>
<tr>
<td></td>
<td>4 hours</td>
<td>80 ppb</td>
<td>1 day a year</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>1 hour</td>
<td>200 ppb</td>
<td>1 day a year</td>
</tr>
<tr>
<td></td>
<td>1 day</td>
<td>80 ppb</td>
<td>1 day a year</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>20 ppb</td>
<td>0</td>
</tr>
<tr>
<td>Lead</td>
<td>1 year</td>
<td>0.50 μg/m³</td>
<td>0</td>
</tr>
<tr>
<td>PM₁₀</td>
<td>1 day</td>
<td>50.0 μg/m³</td>
<td>5 days a year</td>
</tr>
</tbody>
</table>

Table 7: Ambient Air Quality NEPM Standards (EPA 2001)

These NEPM standards are already applicable to the State of Western Australia through the provisions of the National Environment Protection Council (WA) Act 1996. Section 7 of the Act requires WA to put in place the means to ensure that compliance with the NEPM standards is achieved within the 10-year goal (EPA 2001).

5.2.2 Fuel Quality Standards

The introduction of tougher fuel quality standards reduces pollutants in the fuel stream and also allows the implementation of tougher emission standards.
The *Environment Protection (Diesel and Petrol) Regulations 1999* were introduced in Western Australia in January 2000 to reduce vehicle emissions by improving fuel quality. Less stringent national fuel standards were introduced in January 2002. Following the introduction of the less stringent Commonwealth standards, Western Australian fuel standards have been a highly contentious issue and there has been continued pressure to revert to the Commonwealth standards due to perceived pricing and competition impacts of the State regulations (DoE 2005a).

The Commonwealth regulations align fully with the Western Australian regulations in January 2006; this being when Commonwealth fuel standards become increasingly more stringent and thus reducing the likely price difference between WA and the rest of Australia (DoE 2005a). Future fuel policy in WA is aimed at maintaining standards and alignment with future Commonwealth standards from 2006.

### 5.2.3 Emission Standards (ADRs)

Vehicle emission standards specify the maximum concentration of air pollutants from new vehicles, in particular petrol fuelled and diesel fuelled vehicles. Australian vehicle emission standards have always been based on overseas standards and Australia is some years behind Europe in its adoption of most emission standards (Griffith University 2001). The Australian Design Rules will progressively bring Australia’s emission standards into line with European standards.

**Australian Design Rules**

Passenger vehicles manufactured and sold in Australia before 1976 were assumed to have no emissions control equipment. The first Australian Design Rule (ADR) to set emission standards for new vehicles sold in Australia was ADR27, introduced in 1976. Limits were set for hydrocarbon, carbon monoxide, nitrogen oxides and evaporative emissions from petrol-fuelled passenger vehicles with the use of a variety of non-catalytic controls (such as exhaust gas recirculation) (DEP 2002).

Introduced in 1986, ADR37 tightened the limits and made compulsory the use of unleaded petrol. ADR37/01 took effect in 1997, further tightening the limits for emissions from petrol-fuelled vehicles.
ADR79 (equivalent to Euro 2 emissions standard) was implemented in 2003/2004 and ADR79/01 (equivalent to Euro 3) is the current emissions standard on all new petrol vehicles. ADR79/02 will bring Australia in line with the UN Economic Commission for Europe’s (UN ECE) Euro 4 emissions standard. This is expected to be implemented in 2008 (Finucci 2005). Table 8 shows maximum emission limits for new petrol cars for ADR37/01 through to ADR79/02:

<table>
<thead>
<tr>
<th>Standard</th>
<th>Absolute Emission Limits (g/km)</th>
<th>Emissions Test</th>
<th>Other Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Petrol Cars &lt; 2.5t</td>
<td>CO</td>
<td>HC</td>
</tr>
<tr>
<td>ADR 37/01</td>
<td>2.1</td>
<td>0.26</td>
<td>0.63</td>
</tr>
<tr>
<td>ADR 79/00 (Euro 2)</td>
<td>2.2</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>ADR 79/01 (Euro 3)</td>
<td>2.3</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>ADR 79/02 (Euro 4)</td>
<td>1.0</td>
<td>0.1</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 8: Emissions Requirements for Cars (petrol only) (DoTRS 2005)

Despite the impressive reductions in new car emissions, the air quality impacts of motor vehicle emissions continue to be of concern due to several offsetting factors (Rubin 2001):

- Increasing vehicle population,
- Increasing travel per vehicle,
- Departures from governing emission standards, and
- Greater use of 4WDs and light trucks.

For example, the increase in NOX emissions between the 1992/1993 and 1998/1999 reporting period from motor vehicles is predominantly a result of an increase in the number of vehicles and the distance they travel, despite the introduction of more stringent emission standards specified in ADR 37/01 effective from 1997 (DEP 2002).
5.3 CONTROL STRATEGIES

In order to improve air quality in urban environments that are subject to photochemical smog, the quantity of reactants (principally NO\textsubscript{X} and reactive VOCs) emitted into the air must be reduced. Motor vehicles are the largest source of NO\textsubscript{X} and VOCs in the Perth airshed and therefore it is paramount to control and ultimately reduce these emissions.

5.3.1 Motor Vehicle Control

Despite major efforts, adequate control of motor vehicle emissions has proven difficult. Although the emission rate per kilometre has fallen considerably in the last 20 years, the total number of vehicles in use and vehicle kilometres travelled has increased relentlessly thus cancelling out a proportion of potential gains in air quality.

Motor vehicle emissions depend on many factors including fuel quality, engine condition, weather, driver behaviour and effectiveness of emission control device (such as catalytic converters). With the exception of fuel quality, these factors have proven difficult or impossible to control (Kotzias 2001).

5.3.2 Catalytic Converters

In recent decades, control of NO\textsubscript{X} emissions from petrol-powered cars and trucks has been attempted using catalytic converters placed just ahead of the mufflers in the vehicles exhaust system (Baird & Cann 2005).

![Diagram of a Catalytic Converter](Baumbach 1996)
Catalytic converters accomplish a reduction of harmful emissions from the exhaust of a combustion engine through a combination of heat and a precious metal catalyst that causes the harmful emissions to either oxidise or reduce to safe elements in the exhaust flow.

Original two-way converters controlled carbon-containing gases by completing the combustion to carbon dioxide. By use of a surface impregnated with a platinum-rhodium catalyst, the modern three-way converter decomposes nitrogen oxides (NOX) back to elemental nitrogen (N2) and oxygen (O2), using unburned hydrocarbons and the combustion intermediates CO and H2 as reducing agents (Boubel et al. 1994).

The term “three-way” implies that the three pollutants carbon monoxide (CO), nitrogen oxides (NOX) and unburned hydrocarbons are transformed. The following overall reactions occur in the three-way catalyst: (Baumbach 1996)

<table>
<thead>
<tr>
<th>Hydrocarbon Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CnHm + (n + m/4) O2 ⇌ n CO2 + m/2 H2O</td>
</tr>
<tr>
<td>CHm + 2 H2O ⇌ CO2 + (2 + m/2) H2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon monoxide Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + ½ O2 ⇌ CO2</td>
</tr>
<tr>
<td>CO + H2O ⇌ CO2 + H2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduction of Nitrogen oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + CO ⇌ ½ N2 + CO2</td>
</tr>
<tr>
<td>2 (n + m/4) NO + CnHm ⇌ (n + m/4) N2 + m/2 H2O + n CO2</td>
</tr>
<tr>
<td>NO + H2 ⇌ ½ N2 + H2O</td>
</tr>
</tbody>
</table>

The catalyst must come in direct contact with the exhaust gasses for the reaction to take place; therefore if the ceramic becomes clogged or coated with carbon, lead or oil, the converters efficiency is greatly reduced (Baumbach 1996).
5.3.3 Vehicle Inspection and Maintenance Programs

Inspection and maintenance programs have become one of the major initiatives aimed at reducing the output of motor vehicle smog precursors in North America, United Kingdom and other parts of Europe (DEP & Western Power 1996). These programs are intended to ensure that emission characteristics of new vehicles are retained as much as possible. Vehicles not passing the tests are typically denied re-registration until repairs are made to bring emissions within acceptable limits.

Research in Australia has found that although old cars constitute only about 10% of the total car population, they contribute to more than half of the total vehicular emissions, mainly due to the lack of maintenance (Griffith University 2001). Emission control systems are notably unsuccessful in poorly maintained vehicles; a clogged air filter or dirty spark plug can increase hydrocarbon and carbon monoxide emissions well above their normal design limits (Rubin 2001). Old and poorly maintained vehicles that emit high levels of precursor reactants commonly represent a small percentage of the total number of vehicles but they are generally responsible for the greatest part of total vehicle emissions. An effective emissions inspection program encourages improved vehicle maintenance. Furthermore, the cost of owning old vehicles effectively increases and therefore encourages owners to replace their vehicle.

In Western Australia, a State-funded pilot “Petrol Vehicle Emissions Testing Program” commenced in 2003/2004. The aim of this program was to develop a future policy for reducing emissions from petrol vehicles through testing and maintenance, including the replacement of three-way catalytic converters (DoE 2005a). The Perth Air Quality Management Plan - Progress Report (DoE 2005a) delivers an unpromising update stating that “widespread vehicle emissions testing is unlikely to be introduced in Western Australia without external funding of some kind”.

The benefits of implementing a roadside inspections program for light duty vehicles were evident in Sao Paulo where the program was estimated to have reduced emissions of CO by 11%, PM$_{10}$ by 20% and hydrocarbons by 19%. In Santa Fe de Bogota the reductions were estimated at 45% for CO and 55% for hydrocarbons (Elsom 2004). Roadside inspections can be self-funding through the fines imposed on vehicles exceeding mandatory emission limits.
Smoky Vehicle Reporting Program

In November 2002 the introduction of the *Road Traffic (Vehicle Standards) Rules 2002* placed limits on the visible exhaust emissions from vehicles in Western Australia (DoE 2005a). Known as the 10-second rule, it makes it illegal for a vehicle to produce continuous visible smoke for more than 10 seconds. Negotiations are continuing to develop a process for active enforcement for vehicles reported more than five times.

The *Smoky Vehicle Reporting Program* falls seriously short as an effective primary enforcement tool in the hope of reducing car emissions within the Perth urban airshed.
5.4 SMART URBAN PLANNING

Around the world, planning is being undertaken to avoid the ‘car dependence’ phenomenon. Cities are being built and rebuilt to integrate land use with public transport, walking and cycling so that there is a much more balanced transport system and more focused land use.

Reducing the need for travel by redesigning urban community layout and making public transit more efficient and attractive are measures which will be critical in the long-term if vehicle emissions are to be adequately controlled within the Perth airshed.

5.4.1 Urban Community Layout

Under current zoning in Perth, there is the potential for a further 273,000 new homes at relative low density (WAPC & DPI 2004). Continued low-density development will mean that all currently zoned land (and more) will be used up within 30 years.

Progressing with low-density urban development will lead to an increased daily flow of commuters resulting in an increased number and length of journeys made by private motor vehicles. This leads to increased traffic congestion, increased vehicle emissions and increased dependence on motor vehicles. When cheap oil is no longer available, it is the householders in car-dependent outer suburbs that will suffer the most hardship (Parker 2004).

5.4.2 Smarter Public Transit

Promoting walking, cycling and public transport is fundamental to improving air quality in city centres. Urban sprawl often goes ahead at a rate too fast for planners to develop appropriate public transport infrastructure and facilities (Elsom 2004).

Simply providing rail infrastructure needs to be coupled with proactive land use policies encouraging high density activity nodes around rail stations in order to realise the full transit oriented development benefits (WAPC & DPI 2004). In the long term, land use planning and development measures should be used to relieve pressures on a city centre and to create residential urban areas that encourage walking and cycling for short trips and the use of public transport for longer trips.
6. CONCLUSION

Analysis of the latest Perth airshed inventory revealed a 30% increase in NO\textsubscript{X} emissions and an 18% decrease in VOC emissions. Modelling the tropospheric degradation of these emissions reveals a maximum ozone concentration of 148 ppb. This represents an increase of 7 ppb over the 1992/1993 estimated peak ozone concentration. 80 ppb is the limit set by the National Environmental Protection Measures (NEPM) for Ambient Air and concentrations of 148 ppb greatly exceed this. With increasing NO\textsubscript{X} and VOC emissions we can expect to exceed this NEPM limit on a more regular basis throughout the year.

The current trend of emissions projected forward ten years will see maximum ozone concentrations increase to 165 ppb (Scenario #1). Dramatically increasing NO\textsubscript{X} emissions will see maximum ozone concentrations jump to 209 ppb (Scenario #2), whilst reducing NO\textsubscript{X} emissions into the airshed will reduce the maximum ozone concentration down to 142 ppb (Scenario #3).

Motor vehicles have been confirmed as the dominant cause of photochemical smog within the Perth airshed. Aromatic compounds constitute a major component of motor vehicle emissions. Singular aromatic compounds were removed from Scenario #2 and Scenario #3 VOC emissions to determine which species contributed the most to photochemical smog. Tri-methyl benzenes and Xylenes were found to have the biggest potential impact on modelled ozone concentrations within the Perth airshed. VOC-limited Scenario #2 was found to be much more sensitive to the removal of aromatic species as compared to the NO\textsubscript{X}-limited Scenario #3.

To reduce peak ozone concentrations, there is a need to control the dominant source of NO\textsubscript{X} and VOC emissions within the Perth airshed. A combination of policy and technology are successfully reducing motor vehicle emissions by reducing maximum allowed emissions from new vehicles (ADRs) and strict legislation of cleaner fuel quality. Offsetting these advancements is the ever-increasing car population in combination with increased kilometres travelled. Smart urban planning (including improved community layout and effective public transit), together with regular vehicle inspection programs will successfully reduce NO\textsubscript{X} and VOC emissions within the Perth airshed.
7. RECOMMENDATIONS & FURTHER RESEARCH

Modelling Recommendations

To further refine the Perth Airshed Model, the following recommendations are made:

- Test different daily temperatures to determine variation in maximum potential ozone concentrations.
- Calculate accurate humidity parameters for Perth conditions.
- Determine accurate biogenic emission rates in the Perth airshed. Current biogenic emissions for the Perth airshed are very uncertain and require further investigation.
- Experiment with varying emitting areas of the Perth airshed as this has a large effect on emission concentrations.
- Create an ozone isopleth diagram for the Perth airshed. Ozone isopleth diagrams are a critical element in devising effective emission control strategies for regions where current or projected ozone levels exceed air quality standards.
- Compare POCP values of aromatic compounds, appropriate to Perth conditions with the Removal Analysis results. Determine if the most reactive POCP values correspond to Tri-methyl benzenes and Xylenes.
- Investigate (in detail) the Benzene Removal Analysis to determine why ozone profiles increased with removal of this aromatic species.
- Remove two aromatic groups at the same time to determine if overall ozone concentrations decrease/increase by a larger value than the sum of the individual removals (i.e. Remove Xylenes and Tri-methyl benzenes at the same time and determine if overall ozone concentration drops more than 52ppb ⇒ 22ppb for Xylenes and 30ppb for Tri-methyl benzenes).
Recommendations for City of Perth

To reduce emissions from motor vehicles within the Perth airshed, the following two recommendations are made:

- **Implement Vehicle Inspection & Maintenance Program.**
  The benefits of technological and policy-induced improvements (such as tightening emission standards in new cars and the introduction of cleaner fuels) are not fully optimised without ongoing maintenance programs.

  Studies have proven that vehicle inspection and maintenance programs are successful in reducing emissions into the airshed and can be self-funded through the fines imposed on vehicles exceeding mandatory emission limits.

  If the West Australian Government is serious about reducing NO\text{X} and VOC emissions within the Perth airshed, vehicle inspection and maintenance programs must be put into operation.

- **Restrict approvals of sprawling outer-suburbs**
  With an expected 375,000 extra homes in the next 30 years, urban development in Perth needs to get smart. Sprawling outer-suburbs must be minimised at all costs as they lead to car-dependence, traffic congestion and ultimately increased motor vehicle emissions.

  Smart urban planning including development of housing and businesses around transit nodes will encourage the use of other modes of transport such as walking, cycling and public transit.
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Griffith University 2001, *Environmental Pollution (Air Pollution Section)*, Australian School of Environmental Studies.


Lyndon State College, M. D., (9 October 2005), *Earth's Atmospheric Structure* [Online], Available: [http://apollo.lsc.vsc.edu/classes/met130/notes/chapter1/vert_temp_all.html](http://apollo.lsc.vsc.edu/classes/met130/notes/chapter1/vert_temp_all.html) [22 October 2005].


NSC, *Benzene* [Online], Available: [http://nsc.org.library/chemical/benzene.htm](http://nsc.org.library/chemical/benzene.htm) [26/10/05].


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The International Union of Pure and Applied Chemistry, *IUPAC Website* [Online],
### Summary of Annual Emissions of reactive VOC species from the Perth motor vehicle fleet estimated for the 1998/1999 Inventory Year

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kg/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde equivalent</td>
<td>143,584.20</td>
</tr>
<tr>
<td>Acetone</td>
<td>35,895.60</td>
</tr>
<tr>
<td>Acetylene</td>
<td>1,346,101.40</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>71,792.30</td>
</tr>
<tr>
<td>Benzene</td>
<td>902,694.70</td>
</tr>
<tr>
<td>Butane</td>
<td>1,724,241.30</td>
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<tr>
<td>1-Butene</td>
<td>418,097.20</td>
</tr>
<tr>
<td>C4 2-Alkenes</td>
<td>420,577.10</td>
</tr>
<tr>
<td>C5/6 1-Alkenes</td>
<td>487,820.30</td>
</tr>
<tr>
<td>C5/6 2-Alkenes</td>
<td>293,205.10</td>
</tr>
<tr>
<td>Ethane</td>
<td>376,908.30</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>323,063.90</td>
</tr>
<tr>
<td>Ethyl toluene</td>
<td>538,440.40</td>
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<tr>
<td>Ethylene</td>
<td>1,884,543.10</td>
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<tr>
<td>Formaldehyde</td>
<td>323,063.90</td>
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<tr>
<td>Other alkanes</td>
<td>4,979,452.70</td>
</tr>
<tr>
<td>Other aromatics</td>
<td>394,855.80</td>
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<tr>
<td>Pentane</td>
<td>3,035,105.50</td>
</tr>
<tr>
<td>Propane</td>
<td>72,536.60</td>
</tr>
<tr>
<td>Propene</td>
<td>771,765.00</td>
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<tr>
<td>Tolualdehyde</td>
<td>71,792.30</td>
</tr>
<tr>
<td>Toluene</td>
<td>1,810,431.70</td>
</tr>
<tr>
<td>Trimethyl benzene</td>
<td>466,648.70</td>
</tr>
<tr>
<td>Xylene</td>
<td>1,680,743.20</td>
</tr>
</tbody>
</table>
Summary of estimated hourly emissions of criteria pollutants from the Perth motor vehicle fleet for the 1998/1999-inventory period (DEP 2002)

<table>
<thead>
<tr>
<th>Hour of the Day</th>
<th>Total VOC</th>
<th>NOx</th>
<th>CO</th>
<th>SO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>335.73</td>
<td>443.05</td>
<td>3,415.10</td>
<td>10.65</td>
</tr>
<tr>
<td>2</td>
<td>199.76</td>
<td>263.75</td>
<td>2,032.10</td>
<td>6.35</td>
</tr>
<tr>
<td>3</td>
<td>146.46</td>
<td>193.45</td>
<td>1,489.80</td>
<td>4.65</td>
</tr>
<tr>
<td>4</td>
<td>169.03</td>
<td>223.85</td>
<td>1,720.45</td>
<td>5.35</td>
</tr>
<tr>
<td>5</td>
<td>378.82</td>
<td>502.40</td>
<td>3,856.90</td>
<td>12.00</td>
</tr>
<tr>
<td>6</td>
<td>1,249.89</td>
<td>1,659.80</td>
<td>12,727.75</td>
<td>39.65</td>
</tr>
<tr>
<td>7</td>
<td>3,522.15</td>
<td>4,581.60</td>
<td>35,734.25</td>
<td>110.05</td>
</tr>
<tr>
<td>8</td>
<td>4,994.74</td>
<td>6,336.65</td>
<td>50,446.45</td>
<td>153.50</td>
</tr>
<tr>
<td>9</td>
<td>4,414.59</td>
<td>5,669.65</td>
<td>44,688.40</td>
<td>137.00</td>
</tr>
<tr>
<td>10</td>
<td>3,537.71</td>
<td>4,635.55</td>
<td>35,936.20</td>
<td>111.30</td>
</tr>
<tr>
<td>11</td>
<td>3,368.87</td>
<td>4,434.95</td>
<td>34,250.60</td>
<td>106.35</td>
</tr>
<tr>
<td>12</td>
<td>3,426.98</td>
<td>4,510.65</td>
<td>34,841.50</td>
<td>108.20</td>
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<tr>
<td>13</td>
<td>3,479.63</td>
<td>4,579.10</td>
<td>35,376.45</td>
<td>109.90</td>
</tr>
<tr>
<td>14</td>
<td>3,521.10</td>
<td>4,632.55</td>
<td>35,796.95</td>
<td>111.25</td>
</tr>
<tr>
<td>15</td>
<td>3,922.74</td>
<td>5,137.95</td>
<td>39,844.55</td>
<td>123.65</td>
</tr>
<tr>
<td>16</td>
<td>4,701.50</td>
<td>6,084.25</td>
<td>47,653.75</td>
<td>147.05</td>
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<tr>
<td>17</td>
<td>5,036.47</td>
<td>6,500.40</td>
<td>51,021.20</td>
<td>157.30</td>
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<td>18</td>
<td>4,731.10</td>
<td>6,134.00</td>
<td>47,970.05</td>
<td>148.25</td>
</tr>
<tr>
<td>19</td>
<td>3,341.28</td>
<td>4,403.15</td>
<td>33,978.30</td>
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<tr>
<td>20</td>
<td>2,124.60</td>
<td>2,807.70</td>
<td>21,615.60</td>
<td>67.35</td>
</tr>
<tr>
<td>21</td>
<td>1,619.79</td>
<td>2,139.55</td>
<td>16,478.85</td>
<td>51.40</td>
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<tr>
<td>22</td>
<td>1,458.68</td>
<td>1,924.55</td>
<td>14,836.20</td>
<td>46.25</td>
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<tr>
<td>23</td>
<td>1,161.89</td>
<td>1,533.25</td>
<td>11,818.05</td>
<td>36.85</td>
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<tr>
<td>24</td>
<td>737.45</td>
<td>973.10</td>
<td>7,500.75</td>
<td>23.35</td>
</tr>
</tbody>
</table>

61,580.96 kg/day  80,304.90 kg/day  625,030.20 kg/day  1,933.50 kg/day
## APPENDIX C.

### VOC Emission Composition Table

<table>
<thead>
<tr>
<th>VOC Name</th>
<th>VOC CODE</th>
<th>1998/1999</th>
<th>Increased Aromatic Component (25%)</th>
<th>Increased Aromatic Component (49%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>C2H6</td>
<td>17.97</td>
<td>17.97</td>
<td>17.97</td>
</tr>
<tr>
<td>propane</td>
<td>C3H8</td>
<td>15.12</td>
<td>15.12</td>
<td>15.12</td>
</tr>
<tr>
<td>n-butane</td>
<td>NC4H10</td>
<td>19.25</td>
<td>19.25</td>
<td>19.25</td>
</tr>
<tr>
<td>i-butane</td>
<td>IC4H10</td>
<td>8.57</td>
<td>8.57</td>
<td>8.57</td>
</tr>
<tr>
<td>n-pentane</td>
<td>NC5H12</td>
<td>6.74</td>
<td>6.74</td>
<td>6.74</td>
</tr>
<tr>
<td>i-pentane</td>
<td>IC5H12</td>
<td>16.20</td>
<td>16.20</td>
<td>16.20</td>
</tr>
<tr>
<td>n-hexane</td>
<td>NC6H14</td>
<td>1.70</td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>2-methyl pentane</td>
<td>M2PE</td>
<td>4.04</td>
<td>4.04</td>
<td>4.04</td>
</tr>
<tr>
<td>3-methyl pentane</td>
<td>M3PE</td>
<td>2.97</td>
<td>2.97</td>
<td>2.97</td>
</tr>
<tr>
<td>2,3-dimethyl butane</td>
<td>M23C4</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>2,5-dimethyl butane</td>
<td>M25C4</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>n-heptane</td>
<td>NC7H16</td>
<td>1.58</td>
<td>1.58</td>
<td>1.58</td>
</tr>
<tr>
<td>2-methyl hexane</td>
<td>M2HEX</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>3-methyl hexane</td>
<td>M3HEX</td>
<td>1.65</td>
<td>1.65</td>
<td>1.65</td>
</tr>
<tr>
<td>n-octane</td>
<td>NC8H18</td>
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<td>2.25</td>
<td>2.25</td>
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<tr>
<td>n-nonane</td>
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<td>n-undecane</td>
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<td>0.49</td>
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<td>n-dodecane</td>
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<td>0.66</td>
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<td>ethene</td>
<td>C2H4</td>
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<tr>
<td>propene</td>
<td>C3H6</td>
<td>3.91</td>
<td>3.91</td>
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<tr>
<td>but-1-ene</td>
<td>BUT1ENE</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>cis but-2-ene</td>
<td>CBUT2ENE</td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
</tr>
<tr>
<td>trans but-2-ene</td>
<td>TBUT2ENE</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>cis pent-2-ene</td>
<td>CPENT2ENE</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>trans pent-2-ene</td>
<td>TPENT2ENE</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>pent-1-ene</td>
<td>PENT1ENE</td>
<td>1.42</td>
<td>1.42</td>
<td>1.42</td>
</tr>
<tr>
<td>2-methyl-1-butene</td>
<td>ME2BUT1ENE</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>3-methyl-1-butene</td>
<td>ME3BUT1ENE</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td>ME2BUT2ENE</td>
<td>1.12</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>2-methyl propene</td>
<td>MEPROPENE</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
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<td>ethyne</td>
<td>C2H2</td>
<td>10.20</td>
<td>10.20</td>
<td>10.20</td>
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Modelling the effects of Motor Vehicle Emissions on Photochemical Smog in the Perth Airshed
## APPENDIX C.

### VOC Emission Composition Table - CONTINUED

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<th>Compound</th>
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| % AROMATIC SPECIES | 16.4 | 25.3 | 39.7 |


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